

# PATENT ABSTRACTS OF JAPAN

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(71)Applicant : CENTRAL GLASS CO LTD

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(72)Inventor : MAEDA KAZUHIKO  
HIRASHIMA YOSHI  
TSUTSUMI KENTARO

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## (54) FLUORORESIN COATING COMPOSITION

### (57)Abstract:

PURPOSE: To obtain the composition as a film-forming component of coatings capable of providing coating film developing no deterioration/discoloration even under long-term outdoor exposure on buildings and outdoor structures and excellent in weathering resistance and contamination resistance with no rain traces developed.

CONSTITUTION: This coating composition is obtained by incorporating (A) 100 pts.wt. of a fluorocopolymer 100-350mgKOH/g in hydroxyl value produced by copolymerization of a monomer mixture comprising 40-65mol% of chlorotrifluoroethylene, 14-50mol% of a copolymerizable vinyl compound, 16-28mol% of a hydroxyl-contg. polymerizable compound and 0.1-3mol% of a carboxyl-contg. polymerizable compound with (B) 0.05-15 pts.wt. of a water-soluble polyether-modified silicone oil having in the molecule at least dimethylsiloxane structural unit and ethylene oxide structural unit.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the constituent for fluororesin coatings which gave resistance to contamination.

[0002]

[Description of the Prior Art] The fluororesin coating using the weatherability which was excellent in the fluorine system copolymer from the former is manufactured on a commercial basis. The fluorine system copolymer of the solvent meltable mold which recently had at least a hard spot especially is compounded, and many are applied as weatherproof coatings (for example, JP,57-34107,A, JP,61-57609,A, etc.) in fields, such as construction, an automobile, and the chemical industry. Moreover, the drainage system and fine-particles mold coating which thought the environmental side as important and stopped the discharge of an organic solvent are also put in practical use. Principal components are fluorine system raw materials, such as chlorotrifluoroethylene, tetrafluoroethylene, or vinylidene fluoride, and these paint resin increases the solubility of resin by using hydrocarbon system monomers, such as vinyl ester and vinyl ether, as a copolymerization component.

[0003] However, the fault that they tend to become dirty although these solvent meltable mold fluororesin coatings are excellent in weatherability is got. The attempt (a monthly construction finishing technique, VOL19, No 219 and 74 (1993)) which is going to raise soil release nature by making the attempt, and the hydrophilic property and the underwater oil repellency front face which are going to raise surface hardness from making the glass transition point of resin high as the solution means is performed. Neither by the adhesion test of carbon black, nor the dirt test by the magic marker, although contamination-resistant effectiveness is seen, in the actual exposure test, the fluororesin coating which raised surface hardness tends to become dirty too, and has resulted in the clear contamination-resistant improvement.

[0004]

[Problem(s) to be Solved by the Invention] Also in the long-term outdoor exposure which receives [ structure / a building, / outdoor ] this invention, degradation and discoloration of a paint film do not take place, but offers the constituent for fluororesin coatings used as the film formation component of the coating which can form the paint film excellent in the weatherability and the resistance to contamination to which a rain stripe is not attached, either.

[0005]

[Means for Solving the Problem] this invention persons need to make an indispensable monomer hydrocarbon system compounds, such as chlorotrifluoroethylene, vinyl ester, and vinyl ether, the polymerization nature compound of hydroxy group content, and the polymerization nature compound of carboxyl group content at least, as a result of carrying out the stain test of the painted various fluororesin paint films to a detail. To the fluorine system copolymer (A) which has specific OH \*\* which copolymerization is carried out and is obtained, into the molecule, it found out discovering the resistance to contamination excellent in the constituent for coatings which comes to blend the polyether

denaturation silicone oil (B) which has a dimethylsiloxane structural unit and an ethylene oxide structural unit at least, and weatherability, and resulted at this invention.

[0006] At least this invention Namely, 40-65 mol % of chlorotrifluoroethylenes, 14-50 mol % of vinyl system compounds which was chosen from vinyl ester, vinyl ether, and allyl compound ether and which can copolymerize one or more sorts, 16-30 mol % of polymerization nature compounds of hydroxy group content, 0.1-3 mol % of polymerization nature compounds of carboxyl group content It has a dimethylsiloxane structural unit and an ethylene oxide structural unit at least in the fluorine system (copolymer A) 100 weight section whose resin OH \*\* which was made to carry out copolymerization of the monomer mixture which it comes to contain, and was obtained is 100 - 350 mgKOH/g, and a molecule. And the polyether denaturation silicone oil (B) 0.05 which is water solubility - 15 weight sections are blended. It is the becoming constituent for fluororesin coatings.

[0007] This invention is explained to a detail below. In the fluorine system copolymer (A) concerning this invention, chlorotrifluoroethylene takes the 40 - 65-mol range of % of all monomers. In the case of not more than 40 mol %, it is inferior to weatherability, and it falls and is not desirable at more than 65 mol %. [ of the solubility to a solvent ]

[0008] Moreover, although not limited especially as a vinyl system compound which is used for the fluorine system copolymer (A) concerning this invention and which can be copolymerized, vinyl ester, vinyl ether, allyl compound ether, etc. can use it desirably. The ester system compound which there is polymerization nature and has a carbonyl group in a molecule as vinyl ester, for example, vinyl acetate, propionic-acid vinyl, butanoic acid vinyl, vinyl pivalate, caproic-acid vinyl, caprylic-acid vinyl, lauric-acid vinyl, myristic-acid vinyl, palmitic-acid vinyl, stearin acid vinyl, BASA tic 9 acid vinyl, BASA tic 10 acid vinyl, benzoic-acid vinyl, etc. are mentioned. Moreover, as vinyl ether, the methyl vinyl ether, ethyl vinyl ether, butyl vinyl ether, cyclohexyl vinyl ether, etc. are mentioned, for example. Moreover, as allyl compound ether, the ethyl allyl compound ether, the butyl allyl compound ether, the benzyl allyl compound ether, allyl glycidyl ether, the cyclohexyl allyl compound ether, etc. are used, for example. Furthermore, an acrylic ester (meta) system compound, a vinylsilane system compound, etc. are usable. The presentation ratios of these monomers are 14-50-mol% of all monomers. Although there is relation with other copolymerization components, if the solubility to the solvent of a fluorine system copolymer (A) may be inferior and 50-mol % is exceeded, it spoils the weatherability of a paint film and is not desirable less than [ 14 mol % ].

[0009] The allyl compound ether and vinyl ether which have a hydroxy group, or a crotonic-acid denaturation compound can be used for the polymerization nature compound of the hydroxy group content used for the fluorine system copolymer (A) concerning this invention into a molecule. For example, ethylene glycol monoallyl ether, propylene glycol monoallyl ether, Diethylene-glycol monoallyl ether, polyethylene-glycol monoallyl ether, Alkylene glycol monoallyl ether, such as the hydroxy butyl allyl compound ether Hydroxymethyl vinyl ether, hydroxyethyl vinyl ether, Hydroxy butyl vinyl ether, hydroxy pentyl vinyl ether, Crotonic-acid denaturation compounds, such as polyethylene-glycol mono-vinyl ether, such as hydroxyalkyl vinyl ether, such as hydroxy hexyl vinyl ether, and diethylene-glycol mono-vinyl ether, and crotonic-acid hydroxyethyl, etc. are adopted preferably. Furthermore, the glycerol monoallyl ether which has two OH radicals is also suitably adopted into a molecule as a component which can obtain OH \*\* there are few use mols and high. As amount of this glycerol monoallyl ether used, 0.1-30-mol% of all monomers are desirable.

[0010] As a presentation ratio of the polymerization nature compound of these hydroxy group content, it is desirable to take 100 - 350 mgKOH/g and a comparatively high value as OH \*\* of the 16-30-mol fluorine system copolymer (A) of all monomers which is % and is then obtained. If compatibility with polyether denaturation silicone oil (B) falls, and a paint front face does not become smooth and 350 is exceeded, when OH \*\* is less than 100, since faults, such as a soluble fall to a solvent and a compatibility fall with a curing agent, will be discovered, it is not desirable.

[0011] Moreover, especially as a polymerization nature compound of the cull BOKIRU radical content used for the fluorine system copolymer (A) concerning this invention, although not limited, a vinyl acetic acid, a decene acid, undecylenic acid, a crotonic acid, etc. can be mentioned. Although the

polymerization nature compound of this carboxyl group content is useful in order to improve for example, pigment dispersibility and pot life, it becomes [ it is ineffective and / pot life ] short more than at 3 mol % and is not desirable less than [ 0.1 mol % ].

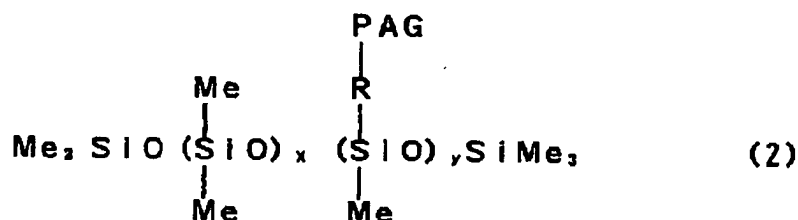
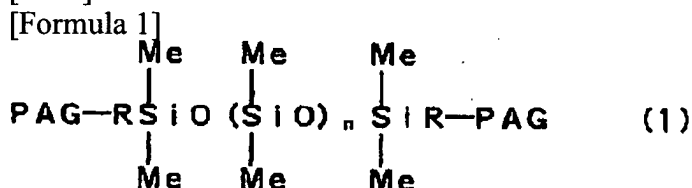
[0012] The polyether denaturation silicone oil (B) used for this invention has a dimethylsiloxane structural unit and an ethylene oxide structural unit at least in a molecule, and is water solubility. Although that does not limit especially such polymerization degree by water solubility, the viscosity in 25 degrees C is about 20-10000cps, and an about 50-3000cps thing is desirable.

[0013] The polyether denaturation silicone oil (B) concerning this invention introduces polyalkylene oxide structure into the piece end, the both ends, or the side chain of poly dimethylsiloxane. As polyalkylene oxide structure, an ethylene oxide structural unit is made indispensable, and otherwise, in arbitration, one sort or two sorts or more can be combined, and it can have the oxy-alkylene structural unit of carbon numbers 3-8. When it has simulataneously two or more sorts of alkylene oxide structural units, the random polymerization of each structural unit may be carried out, and it may be carrying out block polymerization.

[0014] Moreover, although especially the end group of the polyalkylene oxide introduced into the end or side chain of poly dimethylsiloxane is not limited, the polyether denaturation silicone oil (B) concerning this invention also has the case of the functional group which participates in hardening like - OH radical, and can also use these suitably.

[0015] Although it will not be limited especially if the polyether denaturation silicone oil (B) used for this invention suits the conditions described above, what is specifically expressed with the following general formula (1) or (2) is mentioned as a suitable example.

[0016]



[0017] (PAG is a polyalkylene oxide chain including an ethylene oxide structural unit, Me expresses a methyl group and R expresses an alkylene group.) Moreover, n, X, and Y express an integer.

As what is expressed with a general formula (1) when the polyether denaturation silicone oil concerning this invention is enumerated nonrestrictive about a commercial item, SH3746, SF8428, SH3771, BY 16-036, BY 16-027, BY 16-038, and SH8400, SH3749, SH3748 and SF8410 (above, Dow Corning Toray Silicone product.) can be mentioned as what is expressed with SF8427, BY 16-005, BY 16-006, BY 6-007, BY 16-008, and a general formula (2). Moreover, even if it is the product of the other company which is naturally equivalent to these, it cannot be overemphasized that there is same effectiveness.

[0018] In the constituent for fluororesin coatings of this invention, it is desirable to blend polyether denaturation silicone oil (B) 0.05 - 15 weight sections to the fluorine (copolymer A) 100 weight section. Since it will become a thing inferior to weatherability if resistance to contamination sufficient in under the 0.05 weight section is not discovered and 15 weight sections are exceeded, it is not desirable.

[0019] The usual radical polymerization method can be used for the polymerization method of the fluorine system copolymer (A) which is the principal component of this invention in the manufacture, and solution polymerization, a suspension polymerization, and an emulsion polymerization are possible

for it as the polymerization gestalt. Although the temperature of this polymerization process is based on the radical polymerization initiator to be used, it is usually 0-130 degrees C. As a solvent, ester systems, such as ketone systems, such as fluorine systems, such as aromatic hydrocarbon systems, such as saturated hydrocarbon systems, such as alcoholic systems, such as water, t-butanol, and ethyl alcohol, n-hexane, and n-heptane, toluene, and a xylene, trichlorofluoroethane, and dichlorotetrafluoroethane, an acetone, a methyl ethyl ketone, and methyl isobutyl ketone, ethyl acetate, and butyl acetate, etc. are independent, or can use it by mixed stock, for example. As said radical initiator \*\*, for example, diisopropyl peroxy dicarbonate, di-n-propyl peroxy dicarbonate, Dicarboxate, such as di-2-ethylhexylperoxycarbonate Or n-heptafluoro BUCHIRIKKU peroxide, lauroyl peroxy pivalate, Diacyl peroxide, such as t-butyloxy neo decanoate The usual radical initiators, such as peroxy ester, such as alkyl peroxide, such as G t-butyl peroxide and t-butyl cumyl peroxide, t-butylperoxy perpivalate, and t-butylperoxy neodecanoate, can be used.

[0020] Thus, although especially the molecular weight of the fluorine system copolymer (A) by which the polymerization was carried out is not restricted, it is 3000 to about 18000 to use it according to the reinforcement and flexibility of the paint film demanded in 1000-30000 (number average molecular weight; polystyrene conversion) desirable still more preferably. The weatherability and flexibility of a paint film fall the case of 1000 or less, and when it is 30000 or more, the fault which serves as hyperviscosity and is hard to deal with it in coating-izing arises.

[0021] They are that the solvent of the solvent of these fluorine-containing copolymer constituents generally used is independent in the field of coatings, such as an aromatic series system, an ester system, an ether system, a ketone system, and an alcoholic system, or a partially aromatic solvent. Coating-izing is possible for any case like the usual coating, and a pigment and a color can be added suitably.

[0022] Moreover, other additives, for example, an ultraviolet ray absorbent, light stabilizer, a rust-proofer, a dispersant, etc. can be added by the application. It does not restrict melamine system curing agents including the usual urethane system, i.e., a multiple-valued isocyanate system curing agent, especially a block isocyanate system curing agent, etc. as a curing agent, but although it is usable, when using an isocyanate system curing agent, for example, the range of  $\text{NCO}/\text{OH}=0.3-1.0$  is desirable [ the constituent for fluororesin coatings manufactured as mentioned above ]. Moreover, when especially resin OH \*\* is 100 - 350 mgKOH/g, it is desirable that it is in the range of  $\text{NCO}/\text{OH}=0.4-0.7$ . This reason can do a hydrophilic front face by remaining on a paint film front face, without NCO being insufficient and some hydroxy groups participating in a hardening reaction, consequently is considered because a rainfall stops it rain stripe-like to be able to become easily.

[0023] Hereafter, an example explains this invention concretely.

[0024]

[Example]

It is 145g (26-mol %) of vinyl acetate to the SUS nature autoclave of 2l. of inner capacity with one to synthetic example 6 magnetic stirrer, Ethylene glycol monoallyl ether 152g (23-mol %), 12g [ of undecylenic acid ] (one-mol %), and xylene 240g and 13g (Nippon Oil & Fats make) of t-butylperoxy perpivalate were taught, after repeating the degassing permutation 3 times and deaerating it with nitrogen gas, chlorotrifluoroethylene 377g (50-mol %) was taught, and the polymerization was performed at 55 degrees C under the existence of 1.4g of sodium carbonates for 20 hours (synthetic example 1).

[0025] Moreover, the polymerization was performed by the presentation similarly shown in Table 1 (synthetic examples 2-6). After polymerization termination, in any case, contents were taken out and filtered and it used them as the varnish of a fluorine system copolymer (A). OH \*\* in these resin, the acid number, and molecular weight (styrene conversion, number average) are shown in Table 1.

[0026]

[Table 1]

		合成例					
		1	2	3	4	5	6
組成比 モル%	CTFE	50.0	40.0	50.0	50.0	50.0	50.0
	VAc	26.0	10.0	20.0	34.0		20.0
	EVE		23.0			21.0	
	V-9			7.0			
	EGMAE	23.0	20.0	11.0	22.0	15.0	2.0
	GMAE		5.0	11.0		14.0	28.0
	UA	1.0	2.0	1.0	0.3		
OH価, mg/KOH/g		125	182	224	90	271	350
酸価, mg/KOH/g		7.1	12.0	7.4	7.7	—	—
分子量 ( $\times 10^4$ )		0.8	0.9	0.6	1.0	1.2	0.8

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[0027]

CTFE BASA tic 9 acid vinyl EGMAE : Ethylene glycol monoallyl ether GMAE : glycerol monoallyl ether UA : The compound (B) was added at a rate shown in Table 2, respectively to the solid content 100 section of the varnish of the fluorine system copolymer (A) produced in the undecylenic acid example 1 - the examples 1-3 of 7 composition, and it considered as the base resin varnish of a fluorine system coating. : chlorotrifluoroethylene VAc : Vinyl acetate EVE : Ethyl vinyl ether V-9 : The used compounds (B) are Dow Corning Toray Silicone polyether denaturation silicone SF8427 and SH3746 and the polyether denaturation silicone BYK333 made from big KEMI. These have a dimethylsiloxane structural unit and an ethylene oxide structural unit at least in a molecule, and are silicone which is water solubility.

[0028] Next, to the resin 100 section of the base resin varnish which consists of this mixture of (A) and (B), homogeneity mixing of the titanium oxide of the 100 sections was carried out with the distributed mill, and the base resin of a white coating was produced. After adding and carrying out homogeneity mixing so that it may become the rate that NCO/OH shows coronate HX (product made from Japanese Polyurethane Industry) / xylene mixed liquor beforehand mixed to 1:1 to the base resin of this white coating in Table 2, spray painting was carried out to the aluminum plate at the thickness of about 40 microns, and desiccation hardening was carried out for two days in ordinary temperature.

[0029] The stain test and weathering test by static contact angle [ of water ] and outdoor-exposure six months were performed using the paint plate produced by the above. The color difference of the part which does not attach a rain stripe, and the generation condition of a rain stripe performed the judgment of dirt. The result is shown in Table 2. Here, although the pigment was added and (A) and (B) were coating-ized after mixing, also when a curing agent was added after adding the pigment and coating-izing (A) independently, the result was not different from a result in case the procedures in Table 2 differ.

[0030] To the solid content 100 section of the varnish of the fluorine system copolymer (A) produced in the example 1 of a comparison - the examples 4 and 5 of 3 composition, at a rate shown in Table 2, respectively, the compound (B) was added and desiccation hardening was carried out. It considered as the base resin varnish of a fluorine system coating. The used compound (B) is the same as that of an example.

[0031] Then, it considered as the white coating in the same procedure as an example, the coronate HX / the xylene mixed liquor same as a curing agent as an example 1 were added, and it painted to the aluminum plate like the example 1, and was made to dry after paint.

[0032] The stain test and weathering test by static contact angle [ of water ] and outdoor-exposure six months were performed using the paint plate produced by the above. The result is shown in Table 2.

[0033]

[Table 2]

<IMG SRC="/NSAPITMP2/web848/IMAGE/20050209051554681986.gif" WIDTH="392" HEIGHT="415" ALT="ID=000004">

[0034] The <evaluation approach> and contamination-resistant \*\*E : Outdoor-exposure six months were performed and the color difference before and behind exposure (JIS-Z8730) was measured in the part without a rain stripe (an exposure location and Kawagoe, Saitama).

[0035] rain stripe: -- \*\*\*\*\* -- O -- although attached -- \*\*\*\*\* -- O -- although attached, \*\*\*\*\* was comparatively made into x for thin \*\* by \*\* and the deep stripe.

- Weatherability : Accelerated test by sunshine weatherometer 4000 hours (60-degree gloss retention before and behind a trial).

[0036]

[Effect of the Invention] Since it is clear that the outstanding weatherability and the outstanding resistance to contamination that degradation of a paint film does not take place in the weathering test equivalent to a long-term outdoor exposure, and there is no discoloration of a paint film also in an actual extended-outdoor-exposure trial, and a rain stripe is not attached, either are shown as the coating which consists of a constituent for fluororesin coatings of this invention was shown in the example, this constituent for fluororesin coatings is very useful as a film formation component of the coating used for a building, the outdoor structure, etc.

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[Translation done.]



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CLAIMS

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[Claim(s)]

[Claim 1] 14-50 mol % of vinyl system compounds in which 40-65 mol % and copolymerization of chlorotrifluoroethylenes are possible at least, 16-30 mol % of polymerization nature compounds of hydroxy group content, 0.1-3 mol % of polymerization nature compounds of carboxyl group content It has a dimethylsiloxane structural unit and an ethylene oxide structural unit at least in the fluorine system (copolymer A) 100 weight section whose resin OH \*\* which was made to carry out copolymerization of the monomer mixture which it comes to contain, and was obtained is 100 - 350 mgKOH/g, and a molecule. And the constituent for fluoro-resin coatings which comes to blend the polyether denaturation silicone oil (B) 0.05 which is water solubility - 15 weight sections.

[Claim 2] The constituent for fluoro-resin coatings according to claim 1 which are one or more sorts of monomers as which the vinyl system compound which can be copolymerized was chosen from vinyl ester, vinyl ether, and allyl compound ether.

[Claim 3] The constituent for fluoro-resin coatings according to claim 1 with which the polymerization nature compound of hydroxy group content contains the 0.1-30-mol % glycerol monoallyl ether of monomer mixture at least.

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[Translation done.]